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Lithium trialkoxo[tris(trimethylsilyl)methyl]aluminates, analogues of intermediates in reductions of carbonyl compounds. Crystal structures of [Li(thf)$_2$][AlR(OEt)$_3$] and {Li[AlR(OPr^i)$_2$(OH)]}$_2$, R = C(SiMe$_3$)$_3$ and thf = tetrahydrofuran

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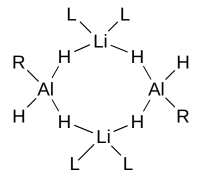
The organotrihydroaluminate [Li(thf)$_2$][(Me$_3$Si)$_3$CAlH$_3$] (thf = tetrahydrofuran) reacted with alcohols R′OH, (R′ = Me, Et, Pr^i or Bu^t), PhOH, aldehydes R^{1}CHO (R^1 = Me, Bu^t or Ph) or ketones R^{1}R^{2}CO (R^1 = R^2 = Me or Ph; R^1 = Me, R^2 = Ph) to give organotrialkoxoaluminates [Li(thf)$_n$][(Me$_3$Si)$_3$CAl(OR′)$_3$] (n = 1, R′ = Me, Pr^i, Bu^t, CH$_2$Bu^t, CH$_2$Ph or CHPh$_2$; n = 2, R′ = Et or Ph; n = 4, R′ = Me), analogues of the intermediates presumed to be present in the reduction of carbonyl compounds by LiAlH$_4$. The structure of [Li(thf)$_2$][(Me$_3$Si)$_3$CAl(OEt)$_3$] was determined by X-ray crystallography which showed that the lithium cation and the organotriethoxoaluminate anion are linked to give a planar LiO$_2$Al ring. The organotrialkoxoaluminates are hydrolysed by traces of water to give organoalkoxohydroxoaluminates and the structure of one of these, {Li[(Me$_3$Si)$_3$CAl(OPr^i)$_2$(OH)]}$_2$, has been determined. The dimer has an Li$_2$Al$_2$O$_6$ framework comprising two adjacent face-sharing cubes with missing atoms at diametrically opposite corners. Terminal and bridging alkoxo groups in solutions of some of these compounds can be distinguished by NMR measurements.

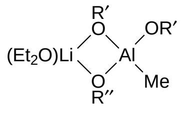
Reductions of aldehydes and ketones with LiAlH$_4$ or related compounds are of considerable importance in organic syntheses.[1–4] Little is known with certainty about the mechanisms of such reactions but it is generally accepted that initial coordination to Li of the oxygen atom of the carbonyl group of the reactant R^{1}R^{2}CO is followed by formation of a complex Li[AlH$_3$OCHR^{1}R^2] in which there are alkoxo and hydride bridges between Li and Al. Further reaction gives the tetraalkoxo-complex Li[Al(OCHR^{1}R^2)$_4$] which can be hydrolysed to the alcohol R^{1}R^{2}CHOH. There is some doubt about whether the initial complex Li[AlH$_3$(OCHR^{1}R^2)] can react directly with further molecules of the carbonyl compound to give Li[AlH$_n$(OCHR^{1}R^2)$_{4-n}$] in which $n = 1$ or 2, and it has been judged to be more likely that Li[AlH$_3$(OCHR^{1}R^2)] gives Li[AlH$_2$(OCHR^{1}R^2)$_2$] and LiAlH$_4$ with the latter as the only attacking species.[5,6] Reductions by Li[AlH(OCHR^{1}R^2)$_3$] are also presumed to proceed by generation of LiAlH$_4$ but the role of the alkoxy group in determining the range of observed reactivity and selectivity is by no means clear.[7]

In view of this background we considered it to be of interest to study the reactions of aldehydes and ketones with lithium organotrihydroaluminates [Li(thf)$_n$][RAlH$_3$] (thf = tetrahydrofuran). Compounds of this type, *e.g.* **1**–**4**, which can be isolated only when they contain bulky organic groups R that prevent conversion into diorganodihydro- and tetrahydro-aluminates,[8,9] have proved to be useful starting materials for further syntheses. Thus the compound [Li(thf)$_2$][(Me$_3$Si)$_3$CAlH$_3$] **1** reacts with a variety of protic reagents HX to give [Li(thf)$_n$][RAlX$_3$] (X = F, OBu^t,[10] SMe or NHPh[11]) or RAlX$_2$·thf (X = Cl, Br, or I),[11] and compound **3**, containing a bulky aryl group, reacts with SiMe$_3$Cl to give RAlH$_x$Cl$_{2-x}$·thf (x = 0–2) and with MeI to give [(RAlH$_2$)$_2$].[12]

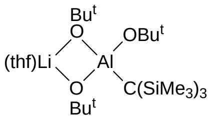
We first made the trialkoxoorganoaluminates [Li(thf)$_n$][RAl(OR′)$_3$] **6**–**10** by the reactions of compound **1** with alcohols or phenol. We then showed that **7a** and **8a** could also be obtained from the appropriate aldehyde or ketone, as could **11**–**13**. As far as we are aware, only two lithium trialkoxoorganoaluminates of this type, **5**[13] and **9**,[10] have been characterised previously by X-ray crystallography. We also describe the partial hydrolysis of [Li(thf)][(Me$_3$Si)$_3$CAl(OPr^i)$_3$] **8a** to give the alkylbis(alkoxo)hydroxoaluminate **14**.



1 R = (Me$_3$Si)$_3$C, L = thf
2 R = (Me$_2$PhSi)$_3$C, L = thf
3 R = 2,4,6-Bu$^t_3$C$_6$H$_2$, L = thf
4 R = 2,4,6-Ph$_3$C$_6$H$_2$ or 2,6-(2,4,6-Me$_3$C$_6$H$_2$)$_2$C$_6$H$_3$, L = Et$_2$O



5 R′ = C$_6$H$_2$Bu$^t_2$-2,6-Me-4, R″ = CMePh$_2$



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6a [Li(thf)][(Me$_3$Si)$_3$CAl(OMe)$_3$]
7a [Li(thf)$_2$][(Me$_3$Si)$_3$CAl(OEt)$_3$]
9 [Li(thf)][(Me$_3$Si)$_3$CAl(OBu^t)$_3$]
11 [Li(thf)][(Me$_3$Si)$_3$CAl(OCH$_2$Bu^t)$_3$]
13 [Li(thf)][(Me$_3$Si)$_3$CAl(OCHPh$_2$)$_3$]
6b [Li(thf)$_4$][(Me$_3$Si)$_3$CAl(OMe)$_3$]
8a [Li(thf)][(Me$_3$Si)$_3$CAl(OPr^i)$_3$]
10 [Li(thf)$_2$][(Me$_3$Si)$_3$CAl(OPh)$_3$]
12 [Li(thf)][(Me$_3$Si)$_3$CAl(OCH$_2$Ph)$_3$]
14 {Li[(Me$_3$Si)$_3$CAl(OPr^i)$_2$(OH)]}$_2$

Experimental

Air and moisture were excluded as far as possible from all reactions by the use of Schlenk-tube techniques and Ar as blanket gas. Reagents and solvents were dried by standard procedures and distilled immediately before use. The light petroleum had b.p. 40–60 °C. Phenol was recrystallised twice from light petroleum; we were unable to obtain a clean product from phenol which had been freshly sublimed. Benzophenone was used as received. The NMR spectra from samples dissolved in C$_6$D$_6$ were recorded at 300 (^{1}H), 62.88 (^{13}C) and 99.36 MHz (^{29}Si) with shifts given relative to SiMe$_4$; ^{7}Li (97.26) and ^{27}Al (65.22 MHz) shifts are relative to aqueous LiCl and aqueous Al(NO$_3$)$_3$ respectively. The compound [Li(thf)$_2$][(Me$_3$Si)$_3$CAlH$_3$]

1 was prepared as described previously.[8] The water content of hydrated Al$_2$(SO$_4$)$_3$ was determined by thermogravimetric analysis. Infrared spectra were of Nujol mulls.

Preparations

[Li(thf)$_4$][(Me$_3$Si)$_3$CAl(OMe)$_3$] 6b. Methanol (0.048 g, 1.5 mmol) was added to a stirred solution of compound **1** (0.20 g, 0.48 mmol) in a mixture of toluene (10 cm^3) and thf (1 cm^3) at 20 °C. Gas evolution was complete after 1 h. The solvent was then removed to give a white moisture-sensitive powder, m.p. 294 °C, which was judged to be [Li(thf)][(Me$_3$Si)$_3$CAl(OMe)$_3$] **6a** (Found: C, 47.9; H, 10.4. C$_{17}$H$_{44}$AlLiO$_4$Si$_3$ requires C, 47.4; H, 10.2%), $\tilde{\nu}_{max}$/cm^{-1} 1257m, 1100m (br), 1050 (sh), 861s and 678w. This powder was not soluble in hydrocarbons but dissolved when a little thf was added. The crystals obtained from light petroleum–thf (100 : 1) seemed from the integration of the signals in the ^{1}H NMR spectrum to be [Li(thf)$_4$][(Me$_3$Si)$_3$-CAl(OMe)$_3$] **6b** (0.12 g, 60%); δ_H 0.51 (27 H, s, MeSi), 1.36, 3.53 (16 H, m, thf) and 3.71 (9 H, s, OMe); δ_C 6.1 (MeSi), 25.6, 67.9 (thf) and 51.2 (OMe); δ_{Li} −0.46; δ_{Al} 90 ($\Delta\nu_{\frac{1}{2}}$ 1250 Hz), δ_{Si} −3.7. However, when kept under vacuum or above 125 °C at 1 atm pressure (101 325 Pa), they lost thf to give the insoluble white powder, **6a**.

[Li(thf)$_2$][(Me$_3$Si)$_3$CAl(OEt)$_3$] 7a. *Method a.* Ethanol (0.072 g, 1.53 mmol) was added to a stirred solution of compound **1** (0.165 g, 0.40 mmol) in a mixture of toluene (10 cm^3) and thf (1 cm^3) at room temperature. After gas evolution had ceased the solvent was removed and the oily residue dissolved in heptane (10 cm^3). The solution was cooled to −20 °C to give colourless moisture-sensitive crystals of **7a** (0.11 g, 52%), m.p. 129 °C (Found: C, 52.0; H, 10.6. C$_{24}$H$_{58}$AlLiO$_5$Si$_3$ requires C, 52.9; H, 10.7%); $\tilde{\nu}_{max}$/cm^{-1} 2723w, 1250m, 1112m, 1075s, 1048s, 911m, 863s, 787m, 751w, 664m and 641m; δ_H 0.59 (27 H, s, MeSi), 1.18 (9 H, t, Et), 4.00 (6 H, q, Et), 1.30, 3.40 (8 H, m, thf); δ_C 6.3 (MeSi), 20.9, 57.9 (Et), 25.5, 68.0 (thf); δ_{Li} −0.34; δ_{Al} 89 ($\Delta\nu_{\frac{1}{2}}$ 970 Hz); δ_{Si} −3.8.

Method b. Acetaldehyde (0.28 cm^3, 5.0 mmol) was slowly added to a stirred solution of compound **1** (0.30 g, 0.95 mmol) in toluene (10 cm^3) at 0 °C. After 2.5 h the solvent was removed and the residue recrystallised from light petroleum (5 cm^3) to give crystals of **7a** (0.24 g, 47%) with spectra identical to those from samples prepared by Method a.

When 2 equivalents of the cyclic ether 12-crown-4 (1,4,7,10-tetraoxacyclododecane) were added to a solution of compound **7a** in toluene and the mixture was cooled to −20 °C crystals of unchanged crown ether separated, leaving a solution which was judged from its ^{1}H NMR spectrum to contain [Li(12-crown-4)][(Me$_3$Si)$_3$CAl(OEt)$_3$] **7b**; δ_H 0.69 (27 H, s, MeSi), 1.48 (9 H, t, Et), 3.16 (16 H, s, crown) and 4.18 (6 H, q, Et).

[Li(thf)][(Me$_3$Si)$_3$CAl(OPr^i)$_3$] 8a. *Method a.* Propan-2-ol (0.20 cm^3, 2.61 mmol) was added to a stirred solution of compound **1** (0.32 g, 0.78 mmol) in toluene (10 cm^3) at room temperature. After 16 h the solvent was removed and the sticky residue crystallised from light petroleum (5 cm^3) at −20 °C to give colourless air- and moisture-sensitive crystals of **8a** (0.20 g, 50%), m.p. 70°C (Found: C, 53.2; H, 10.7. C$_{23}$H$_{56}$AlLiO$_4$Si$_3$ requires C, 53.7; H, 10.9%); $\tilde{\nu}_{max}$/cm^{-1} 1257m, 1177s, 1163s, 1138s, 1046s, 1018s, 992s, 862vs, 666s and 603s; δ_H 0.57 (27 H, s, MeSi), 1.12, 3.25 (4 H, m, thf), 1.25 (18 H, d, Pr^i) and 4.47 (3 H, spt, Pr^i); δ_C 6.2 (MeSi), 25.4, 68.3 (thf), 28.2, 63.3 (Pr^i); δ_{Li} 0.0; δ_{Al} 84, $\Delta\nu_{\frac{1}{2}}$ 780 Hz; δ_{Si} −4.0.

Method b. Acetone (0.15 cm^3, 2.04 mmol) was added to a solution of compound **1** (0.22 g, 0.53 mmol) in toluene (10 cm^3) at 20 °C. The mixture was stirred for 16 h, then the solvent was removed and the residue recrystallised from light petroleum–thf (10 : 1, 11 cm^3) to give colourless crystals of **8a** (0.22 g, 81%) identical with those prepared by Method a.

When 2 equivalents of tmen (Me$_2$NCH$_2$CH$_2$NMe$_2$) were added to a solution of compound **8a** in toluene the solid recovered upon recrystallisation was shown by its ^{1}H NMR spectrum to have the composition [Li(tmen)$_n$][(Me$_3$Si)$_3$CAl-(OPr^i)$_3$] **8b** with $n = 1$ and not the expected 2.

[Li(thf)][(Me$_3$Si)$_3$CAl(OBu^t)$_3$] 9. The synthesis of this compound has been described previously.[10]

[Li(thf)$_2$][(Me$_3$Si)$_3$CAl(OPh)$_3$] 10. A solution of phenol (0.28 g, 3.0 mmol) in toluene (10 cm^3) was added to a stirred solution of compound **1** (0.40 g, 0.97 mmol) in toluene (20 cm^3) and the mixture was stirred for 18 h at room temperature. The solvent was removed, the sticky residue extracted into light petroleum (10 cm^3), the extract filtered, and the filtrate cooled to −20 °C to give colourless moisture-sensitive crystals of **10** (0.15 g, 22%), m.p. 115 °C (Found: C, 62.9; H, 8.4. C$_{36}$H$_{58}$AlLiO$_5$Si$_3$ requires C, 62.8; H, 8.4%); $\tilde{\nu}_{max}$/ cm^{-1} 1924m, 1851w, 1779w, 1712w, 1594s, 1261s, 1168m, 1122w, 1070m, 1041s, 999m, 861s, 802s, 758m, 638w and 612w; δ_H 0.51 (27 H, s, Me), 1.07, 3.06 (8 H, m, thf), 6.79 (3 H, m, *p*-H), 7.11–7.13 (12 H, m, *o*-, *m*-H); δ_C 6.2 ($J_{SiC} = 50$ Hz, Me), 25.0, 68.4 (thf), 119.4 (*p*-C), 120.7 (*o*-C), 129.7 (*m*-C), 158.7 (*ipso*-C); δ_{Li} −0.6; δ_{Al} 76, $\Delta\nu_{\frac{1}{2}}$ 3.2 kHz; δ_{Si} −3.3.

[Li(thf)][(Me$_3$Si)$_3$CAl(OCH$_2$Bu^t)$_3$] 11. 2,2-Dimethylpropanal (0.50 cm^3, 4.60 mmol) was added to a stirred solution of compound **1** (0.31 g, 0.75 mmol) in toluene (10 cm^3) at room temperature. After 16 h the solvent was removed under vacuum and the residue recrystallised from light petroleum (5 cm^3) at −20 °C to give colourless blocks of **11** (0.22 g, 49%), m.p. 167 °C (Found: C, 57.7; H,11.3. C$_{29}$H$_{68}$AlLiO$_4$Si$_3$ requires C, 58.2; H, 11.4%); $\tilde{\nu}_{max}$/cm^{-1} 2708w, 1397m, 1364s, 1255s, 1243s, 1175m, 1119s, 1078vs, 1034s, 1024s, 861vs, 790m, 768m, 738m, 674s and 665s; δ_H 0.58 (27 H, s, SiMe$_3$), 0.98 (27 H, s, Bu^t), 1.12, 3.29 (4 H, m, thf) and 3.76 (6 H, q, OC*H*$_2$Bu^t); δ_C 6.5 ($J_{SiC} = 50$ Hz, SiMe$_3$), 25.0, 68.8 (thf), 27.0 [C(*C*H$_3$)$_3$], 33.4 [*C*(CH$_3$)$_3$] and 74.6 (*C*H$_2$Bu^t); δ_{Li} −0.34; δ_{Al} 93, $\Delta\nu_{\frac{1}{2}}$ 1560 Hz; δ_{Si} −3.9.

[Li(thf)][(Me$_3$Si)$_3$CAl(OCH$_2$Ph)$_3$] 12. Benzaldehyde (0.33 cm^3, 3.25 mmol) was added dropwise to a stirred solution of compound **1** (0.45 g, 1.09 mmol) in toluene (20 cm^3) at room temperature. After 18 h the solvent was removed under vacuum from the pale yellow solution to leave a viscous residue (0.72 g, 100%). Attempts to crystallise this were unsuccessful, but it was judged from spectroscopic data to be **12**; $\tilde{\nu}_{max}$/cm^{-1} 3063w, 3027w, 1658w, 1604w, 1495m, 1253s, 1209m, 1122m, 1067s, 1042m, 1028m, 862vs, 791m, 754m, 703s and 667s; δ_H 0.62 (27 H, s, Me), 1.01, 2.84 (4 H, m, thf), 5.07 (6 H, s, OCH$_2$), 7.06–7.35 (15 H, m, Ph); δ_C 6.1 (Me), 24.8, 67.6 (thf), 66.2 (OCH$_2$), 126.9 (*p*-C), 127.3 (*o*-C), 128.7 (*m*-C), 145.2 (*ipso*-C); δ_{Li} −0.77; δ_{Al} 89, $\Delta\nu_{\frac{1}{2}} = 2740$ Hz; δ_{Si} −3.7.

[Li(thf)][(Me$_3$Si)$_3$CAl(OCHPh$_2$)$_3$] 13. A solution of benzophenone (0.40 g, 2.2 mmol) in toluene (5 cm^3) was slowly added to a stirred solution of compound **1** (0.30 g, 0.73 mmol) in toluene (20 cm^3) at room temperature. After 14 h the solvent was removed under vacuum and the sticky residue washed with light petroleum (2 × 2 cm^3), then crystallised from toluene (3 cm^3) at −20 °C to yield colourless moisture-sensitive crystals of **13** (0.35 g, 55%), m.p. 184 °C (Found: C, 71.0; H, 7.6. C$_{53}$H$_{68}$AlLiO$_4$Si$_3$ requires C, 71.8; H, 7.7%); $\tilde{\nu}_{max}$/cm^{-1} 1597m, 1491m, 1352w, 1313w, 1249s, 1188m, 1105s, 1065s, 1043s, 1024s and 917s; δ_H 0.38 (27 H, s, Me), 1.09, 3.08 (4 H, m, thf), 6.16 (3 H, s, CH), 7.02–7.33 (30 H, m, Ph); δ_C 6.5 (Me), 25.1, 68.6 (thf), 77.7 (CH), 126.8 (*p*-C), 127.4 (*o*-C), 128.5 (*m*-C) and 148.2 (*ipso*-C); δ_{Li} 0.5; δ_{Al} 97, $\Delta\nu_{\frac{1}{2}}$ 3.42 kHz; δ_{Si} −4.1.

{Li[(Me$_3$Si)$_3$CAl(OPr^i)$_2$(OH)]}$_2$ 14. A solution of [Li(thf)]-[(Me$_3$Si)$_3$CAl(OPr^i)$_3$] **8a** (0.100 g, 0.19 mmol) in toluene (20 cm^3) was stirred with Al$_2$(SO$_4$)$_3$·15H$_2$O (0.19 mmol H$_2$O) for

22 h at 20 °C. The ^{1}H NMR spectrum showed that **8a** had disappeared and that no $(Me_3Si)_3CH$ had been formed. The solvent was pumped away and the residue stirred with light petroleum (10 cm^3). The clear solution was filtered and the filtrate concentrated and cooled to −20 °C to give **14** as colourless needles (0.049 g, 64%), m.p. 194 °C (Found: C, 47.6; H, 10.3. $C_{16}H_{42}AlLiO_3Si_3$ requires C, 48.0; H, 10.5%); $\tilde{\nu}_{max}/cm^{-1}$ 3753m, 3700m, 2722w, 2639w, 1912m, 1855m, 1609m, 1261s, 1143s (br), 1019s and 796w; δ_H 0.41 (27 H, s, MeSi), 1.20 (12 H, d, Pr^i), 3.85 (1 H, s, OH), 4.31 (2 H, spt, Pr^i); δ_C 6.3 (MeSi), 28.1, 63.4 (Pr^i); δ_{Li} −0.17; δ_{Al} 92, $\Delta\nu_{\frac{1}{2}}$ 2858 Hz; δ_{Si} −4.4.

Reaction of compound 1 with acetophenone. The NMR spectrum of a mixture obtained from the reaction of compound **1** with acetophenone showed the presence of four signals in each of the methyl and methine regions indicating that the various stereochemically distinct species had been formed in similar amounts.

Reaction of compound 8a with benzophenone. A mixture of compound **8a** (0.70 mmol) and Ph_2CO (2.1 mmol) was heated under reflux in benzene (20 cm^3) and half of the solvent was then slowly distilled off. After 3 h the mixture was allowed to cool. The ^{1}H NMR spectrum showed only signals from $[Li(thf)][(Me_3Si)_3CAl(OPr^i)_3]$ **8a** and Ph_2CO and none assignable to $[Li(thf)][(Me_3Si)_3CAl(OCHPh_2)_3]$ **13**.

Crystallography

Crystal data. $C_{24}H_{58}AlLiO_5Si_3$ **7a**, $M = 544.9$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 12.413(3)$, $b = 15.690(4)$, $c = 17.337(5)$ Å, $U = 3377$ Å^3, $\lambda = 0.710\,73$ Å, $Z = 4$, $D_c = 1.07$ Mg m^{-3}, $F(000) = 1200$, colourless, air-sensitive block, 0.3 × 0.3 × 0.3 mm, μ(Mo-Kα) = 0.19 mm^{-1}, $T = 173(2)$ K.

$C_{32}H_{84}Al_2Li_2O_6Si_6$ **14**, $M = 801.4$, monoclinic, space group $P2_1/c$ (no. 14), $a = 12.765(3)$, $b = 10.841(11)$, $c = 18.626(10)$ Å, $\beta = 105.81(4)°$, $U = 2480(3)$ Å^3, $\lambda = 0.710\,73$ Å, Z = 2, $D_c = 1.07$ Mg m^{-3}, $F(000) = 880$, colourless, air-sensitive block, 0.4 × 0.4 × 0.3 mm, μ(Mo-Kα) = 0.24 mm^{-1}, $T = 173(2)$ K.

Data collection. Data were collected on an Enraf-Nonius CAD4 diffractometer in the θ–2θ mode with Mo-Kα radiation and $2 < \theta < 25°$; 3333 independent reflections were used for compound **7a** and 3418 for **14**. Absorption or decay corrections were not applied.

Structure analysis and refinement. The structures were solved by direct methods (SHELXS 86)[14] and refined by full-matrix least squares on all F^2 (SHELXL 93)[15] with all non-hydrogen atoms anisotropic. Hydrogen atoms were included in the riding mode with $U_{iso} = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$ for Me groups. For compound **7a** the Si atoms were disordered over two sets of positions with occupancies 0.76 : 0.24; methyl hydrogens for the lower-occupancy orientation were omitted. For 1875 reflections with $I > 2\sigma(I)$, $R1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.081$; $wR2$ (all data) = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}} = 0.289$. The large anisotropic displacement factors for some carbon atoms probably indicate unresolved disorder in the conformations of the thf rings. For **14** the hydroxyl H atom was located on a difference map and freely refined isotropically. For 3418 reflections with $I > 2\sigma(I)$, $R1 = 0.044$; $wR2$ (all data) = 0.118.

CCDC reference number 186/748.

Discussion

The trihydroaluminate $[Li(thf)_2][RAlH_3]$ **1** $[R = (Me_3Si)_3C]$ reacted with alcohols to give a series of trialkoxoaluminates $[Li(thf)_n][RAl(OR')_3]$ **6**–**10**, which were isolated as crystalline solids. The ethoxo and isopropoxo derivatives, **7a** and **8a**, were also obtained from the reactions of **1** with acetaldehyde and acetone, respectively, and the 2,2-dimethylpropoxo, benzoxo and diphenylmethoxo compounds, **11**–**13**, were likewise made from the appropriate carbonyl compounds. (In toluene solution at room temperature there is no attack on the Al–C bond, presumably because this is protected by the bulky substituent R at aluminium.) The thf : Al ratio n depends on the size of the alkoxo group OR′. The trimethoxo derivative was isolated as a white powder, **6a**, which appeared from analyses (C, H) to have $n = 1$. The powder was insoluble in hydrocarbons but it dissolved in toluene containing small amounts of thf, and the ^{1}H NMR spectrum of a solution containing insufficient thf to dissolve the whole sample showed that the species in solution had $n = 4$. Crystals isolated from light petroleum–thf readily lost thf to leave the powder **6a** with $n = 1$. The insolubility of **6a** in hydrocarbons suggested that it might have a polymeric structure unlike those of the other trialkoxoaluminates described here. The ^{1}H NMR spectrum of **6b** suggested that it might be an unbridged ate complex with the ionic formula $[Li(thf)_4][RAl(OMe)_3]$ but attempts to isolate similar complexes with R′ = Et or Pr^i were unsuccessful. The triethoxo compound $[Li(12\text{-crown-}4)][RAl(OEt)_3]$ **7b**, rather than $[Li(12\text{-crown-}4)_2][RAl(OEt)_3]$, was obtained from a mixture of the triethoxo derivative **7a** and a two-fold excess of the crown ether (both types of complex are known with other counter anions[16]). Likewise, crystals of the isopropoxo derivative $[Li(tmen)][RAl(OPr^i)_3]$ **8b**, not $[Li(tmen)_2][RAl(OPr^i)_3]$, separated from light petroleum in the presence of an excess of tmen. These observations suggest that the aluminate ions $[RAl(OR')_3]^-$ successfully compete with ether or amine donors for sites in the co-ordination sphere of lithium. In the derivatives with R′ = Pr^i, Bu^t, CH_2Bu^t, CH_2Ph or $CHPh_2$ there was apparently room for only one co-ordinated thf molecule. In each case all three Al–H bonds in $[Li(thf)_2][(Me_3Si)_3CAlH_3]$ were converted into Al–O bonds in the alkoxoaluminate product. The NMR spectra of mixtures obtained by the addition of 1 or 2 equivalents of EtOH to **1** showed that **1**, **7a** and two other aluminate species were present, suggesting that, under the conditions of the experiment, the ions $[RAlH_3]^-$, $[RAlH_2(OEt)]^-$, $[RAlH(OEt)_2]^-$ and $[RAl(OEt)_3]^-$ were all present.

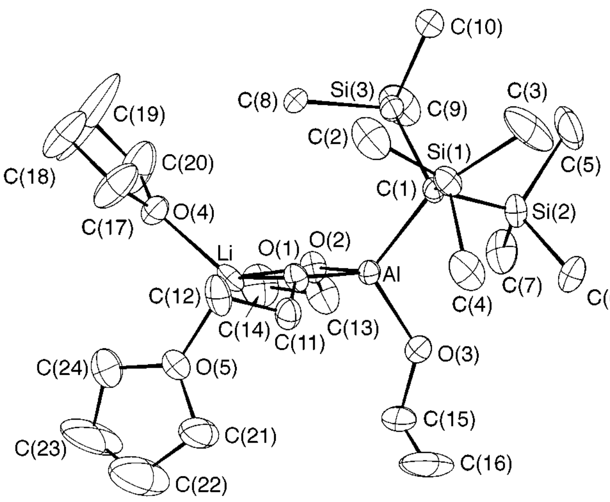

Fig. 1 Molecular structure of compound **7a**

The molecular structure of $[Li(thf)_2][(Me_3Si)_3CAl(OEt)_3]$ **7a** is shown in Fig. 1, and selected bond lengths and angles in **7a** and $[Li(thf)][(Me_3Si)_3CAl(OBu^t)_3]$ **9**[10] are listed in Table 1. The Li–O and Al–O distances are similar to those in the aryloxo compound **5**.[13] The Li–O distances are on the long side but within the usual range.[17] As expected, the terminal Al–O distances are shorter than the bridging distances but the difference is smaller than that found in dimeric alkoxides.[18] The molecules therefore appear to be tight lithium tri(alkoxo)aluminate ion pairs with alkoxo bridges between Li and Al. The LiO_2Al ring is planar (sum of angles 359.8°) in the ethoxo compound **7a** and

Table 1 Bond lengths (Å) and angles (°) in $[Li(thf)_2][RAl(OEt)_3]$ **7a**, $[Li(thf)][RAl(OBu^t)_3]$ **9**[10] and $\{Li[RAl(OPr^i)_2(OH)\}_2$ **14** $[R = C(SiMe_3)_3]$

	7a	**9**	**14**
Al–O(1)	1.776(6)	1.789(7)	1.760(2)
Al–O(2)	1.776(6)	1.788(7)	1.765(2)
Al–O(3), Al–OH[a]	1.738(7)	1.698(7)	1.779(2)[a]
Al–C(R)	2.014(9)	2.031(11)	1.996(3)
Li–O(1)	1.89(2)	1.94(2)	1.989(4)
Li–O(2)	1.93(2)	1.97(2)	2.011(4)
Li–thf, Li–OH[a]	1.96(2), 1.97(2)	1.95(2)	1.996(5), 1.957(5)[a]
Mean Si–C	1.875(10)	1.887(11)	1.883(3)
Mean Si–Me	1.906(12)	1.879(11)	1.876(3)
O(1)–Li–O(2)	82.3(7)	82.2(7)	*b*
O(2)–Li–thf	119.7(9), 118.4(9)	138.6(12)	
O(1)–Li–thf	124.6(9), 116.4(9)	137.1(12)	
O(1)–Al–O(2)	90.2(3)[c]	92.0(3)[c]	111.0(1)[d]
O(1)–Al–O(3)	112.8(4)[d]	114.8(4)[d]	92.3(1)[a,c]
O(2)–Al–O(3)	112.1(4)[d]	117.9(4)[d]	91.6(1)[a,c]
O(1)–Al–C (R)	116.5(4)	107.8(4)	119.4(1)
O(2)–Al–C (R)	116.7(4)	109.9(4)	120.7(1)
O(3)–Al–C (R)	107.9(4)	112.5(4)	114.5(1)[a]
Al–O(1)–Li	94.3(6)	92.1(7)	93.2(2)[e]
Al–O(2)–Li	93.0(6)	91.3(6)	92.2(2)[e]
Al–O(1)–C (R′)	130.1(6)	138.8(5)	143.8(2)
Al–O(2)–C (R′)	129.5(7)	142.4(6)	141.3(2)
Al–O(3)–C (R′)	130.1(8)	167.4(8)	
Li–O(1)–C (R′)	125.0(8)	112.5(8)	121.3(2)
Li–O(2)–C (R′)	125.6(7)	114.7(8)	124.0(2)
Mean Si–C–Si	111.0(4)	108.2(6)	110.4(2)
Mean Me–C–Me	106.3(6)	104.2(5)	104.9(2)
Mean Al–C–Si	107.8(4)	110.7(5)	108.4(2)

[a] In compound **14** O(3) is the oxygen atom in the μ_3-OH group. [b] Endocyclic angles: O(1)–Li–O(3) 79.6(2), O(2′)–Li–O(3′) 79.6(2), O(3)–Li–O(3′) 95.6(2)°. Exocyclic angles: O(1)–Li–O(2′) 172.9(2), O(3)–Li–O(2′) 105.1(2), O(1)–Li–O(3′) 105.5(2)°. [c] Endocyclic. [d] Exocyclic. [e] Li–OH–Al 93.6(2), 92.4(2), Li–OH–Li′ 84.4(2)°.

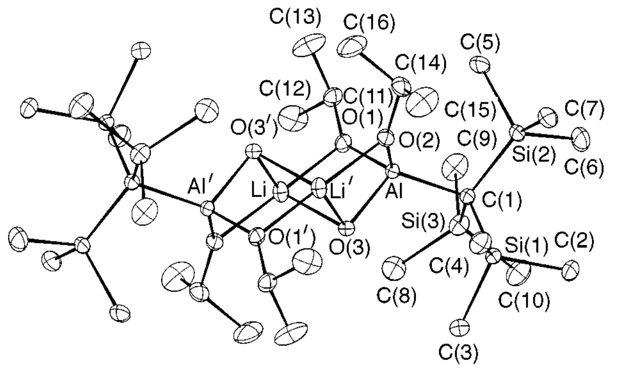

Fig. 2 Molecular structure of compound **14**

almost so in the *tert*-butoxo derivative **9** (sum of angles 357.6°). The bridging ethoxo groups and the thf molecules co-ordinated to lithium are all pushed away from the bulky group R, so that C(11) and C(13) are on the opposite side of the ring to C(1) and the O(1)–Li–O(4) angle is greater than O(1)–Li–O(5). Similar steric effects are observed in **9**. In **7a** the O–C bonds of the bridging alkoxo groups are at about 90° to the Li · · · Al axis, but in **9** they are bent away from the large group attached to aluminium and pushed towards the lithium, which has only one co-ordinated thf molecule, instead of two. The congestion arising from the bulky Bu^t groups is also shown by the fact that the Li–μ-OR′ bonds are slightly shorter in **7a**, in which Li is four-co-ordinate, than they are in **9**, in which Li is three-co-ordinate. The C–O (terminal)–Al angle in **9** [167.4(8)°] is much wider than that in **7a** [130.1(8)°].

The NMR spectra for the ethoxo, *tert*-butoxo, 2,2-dimethylpropoxo and diphenylmethoxo compounds **7a**, **9**, **11** and **13**, respectively, at room temperature showed only one set of peaks attributable to alkoxo protons, indicating that bridging and terminal groups were exchanging rapidly on the NMR time-scale. Separate signals were observed from samples at low temperatures and the free energies of activation were calculated from the coalescence temperatures and the chemical shifts under conditions of slow exchange. The values of $\Delta G^{\ddagger}$/kJ mol^{-1} were 48.2 for **7a**, 47.5 for **11** and 44.6 for **13** but 62.3 for the significantly more crowded Bu^t compound **9**. The simplest process for exchange involves breaking only one Li–O bond and reforming the ring with a different alkoxo group in the bridge position. Since the crystallographic data (see Table 1) suggest that the Li–O bond in the *tert*-butoxo derivative **9** is a little longer and weaker than that in the ethoxo compound **7a** it appears that the slower bridge–terminal exchange in **9** results from significantly greater steric interactions between Bu^t and $SiMe_3$ groups.

Experiments in NMR tubes showed that when water was added to toluene solutions of the trialkoxoaluminates **7a**, **8a** or **11** new species containing single $(Me_3Si)_3C$ groups were obtained cleanly without formation of $(Me_3Si)_3CH$. No attempt has been made to characterise these but it is likely that they are alkoxohydroxoorganoaluminates, like the compound $\{Li[RAl(OPr^i)_2(OH)]\}_2$ **14** obtained by treatment of the aluminate $[Li(thf)][RAl(OPr^i)_3]$ **8a**, with hydrated aluminium sulfate (a procedure developed for the synthesis of Bu^t_2AlOH).[19–20] Crystals suitable for an X-ray diffraction study were obtained from benzene. The molecular structure is shown in Fig. 2 and significant bond lengths and angles are given in Table 1. The dimer has a centre of symmetry and the central framework has, within experimental error, a plane of symmetry through the two aluminium atoms and O(3). The framework is of a type that was first found for the tetrameric $\{Ti(OEt)_4\}_4$[21] and has been shown[22] to be widely distributed among both homo-[23–25] and hetero-[26] polynuclear metallic alkoxides, amides,[27] phosphides[28] and halides.[29–31] There do not seem to be any previous examples involving Li and Al although a Li–Sn[26] and a Li–Ga[31] compound have been described. The molecular parameters for **14** are similar to those for **7a** and **9.** The long Li–O and short Al–O distances suggest that the OH and OPr^i groups are more strongly bound to Al than to Li so that the compound is best formulated as a lithium alkylaluminate. An alternative view of the molecular structure is that it is a fragment of the lattice of the hexagonal high-pressure polymorph of $LiAlO_2$[32] with organic groups on the periphery. These prevent the intermolecular elimination of hydrocarbons that is required for the build-up of more extensive Al–O–Li frameworks by keeping apart the Al–C bonds in one molecule and the O–H bonds in another. In a similar way the hydroxobenzoatoaluminium compound $[Al_5Bu^t_5(\mu_3\text{-}O)_2(\mu_3\text{-}OH)_2(\mu\text{-}OH)_2(\mu\text{-}O_2CPh)_2]$ and the *tert*-butylhydroxoaluminium compound $[Al_6Bu^t_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4]$ are related to the mineral boehmite.[33] It is significant that other known organoaluminium hydroxides also contain bulky alkyl groups that prevent condensation to give extended Al–O frameworks.[19,20,34,35]

The alkoxo derivatives described here are related to the intermediates in the reduction of aldehydes or ketones by $LiAlH_4$ and similar compounds, and our results have a bearing on studies to elucidate the mechanisms of such reactions. The following points appear to be relevant. First, the strong co-ordination of the alkoxoaluminate ion to the lithium counter ion in both starting material and product suggests that it is possible that the counter ion is involved in the rate-determining step as is suggested also by kinetic studies.[5] Secondly, all three Al–H bonds are available for reduction even though reaction of $[RAlH_3]^-$ *via* conversion into $[AlH_4]^-$ and $[R_2AlH_2]^-$ is apparently inhibited when R is very large. As mentioned in the introduction, there is doubt about whether the initial monoalkoxoaluminate $Li[AlH_3(OCHR^1R^2)]$ formed in the reaction of a carbonyl compound R^1R^2CO with $LiAlH_4$ can react directly with a further molecule of carbonyl compound or whether alkoxoaluminates give free $[AlH_4]^-$ which then reacts with carbonyl substrate. In our work redistribution of the sterically hindered trihydroorganoaluminates to generate $[AlH_4]^-$ is unlikely but carbonyl compounds nevertheless readily give trialkoxo derivatives. These results suggest that aldehydes and ketones could react directly with trihydroaluminates $[AlH_3(OCHR^1R^2)]^-$ though in the absence of a bulky group attached to aluminium a faster pathway *via* $[AlH_4]^-$ may be available. Thirdly, steric effects from the group R′, as shown by the rate of bridge–terminal exchange, are small when R′ is secondary and become marked only when R′ is tertiary. Fourthly, the stereoselectivity of the reduction of acetophenone by $[RAlH_3]^-$ appears to be low. Fifthly, the species present in solution are affected by traces of water which give oligomeric species with Li–O–Al frameworks. These can be expected to have a marked influence on both the kinetics and the selectivity of lithium aluminium hydride reducing agents.

Since a key step in the important Meerwein–Ponndorf–Verley reaction for conversion of ketones into alcohols in the presence of aluminium isopropoxide is taken to involve displacement of acetone from $Al{-}OCHMe_2$ by a ketone R_2CO to give $Al{-}OCR_2H$, we thought it would be of interest to see whether a less-volatile ketone would displace acetone from the tris(isopropoxo)aluminate **8a**. However, when a mixture of benzophenone and **8a** was heated in benzene under conditions in which acetone could be distilled away only unchanged starting materials were recovered. Reaction is apparently precluded either by steric hindrance from the large alkyl group attached to aluminium or because essential three-co-ordinate aluminium centres[36] are formed less readily from **8a** than from oligomeric aluminium isopropoxide itself.

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